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(19) (CA) **CANADIAN PATENT** (12)

(54) Abrasion Resistant Ultraviolet Light Curable Hard
Coating Compositions

(72) Chung, Rack H.,
U.S.A.

(73) Granted to General Electric Company
U.S.A.

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ABRASION RESISTANT ULTRAVIOLET LIGHT
CURABLE HARD COATING COMPOSITIONS

Field of the Invention

This invention relates to photocurable hard
5 coating compositions, and articles coated with such
compositions. These coatings are comprised of the
photoreaction products of certain multifunctional
acrylate ester monomers or mixtures thereof which are
catalyzed with a blend of photoinitiators comprised of
10 photosensitive ketones and certain hindered amines,
which are effective for crosslinking the acrylate ester
monomers upon exposure to ultraviolet radiation. The
process of the present invention specifically does not
require an inert atmosphere such as nitrogen and may in
15 fact be carried out in air.

More particularly, this invention relates to an
article having a photocured coating thereon which is mar,
abrasion, and solvent resistant, has good adhesion to the
substrate, and is compatible with the substrate i.e., does
20 not adversely affect the substrate by stress cracking and
crazing it, by causing crack propagation into the substrate
as a result of brittleness of the coating itself, and/or
by adversely affecting the properties of the substrate
generally such as, for example, impact resistance,
25 elongation, and tensile strength.

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Background of the Invention

Recently, the substitution of glass glazing with transparent materials which do not shatter or are more resistant to shattering than glass, has become widespread. For example, transparent glazing made from synthetic organic polymers is now utilized in public transportation vehicles, such as trains, buses, taxis and airplanes. Lenses, such as for eye glasses and other optical instruments, as well as glazing for large buildings, also employ shatter-resistant transparent plastics. The lighter weight of these plastics in comparison to glass is a further advantage, especially in the transportation industry where the weight of the vehicle is a major factor in its fuel economy.

While transparent plastics provide the major advantage of being more resistant to shattering and lighter than glass, a serious drawback lies in the ease with which these plastics mar and scratch, due to everyday contact with abrasives, such as dust, cleaning equipment and ordinary weathering. Continuous scratching and marring results in impaired visibility and poor aesthetics, and often requires replacement of the glazing or lens or the like.

One of the most promising and widely used transparent plastics for glazing is polycarbonate, such as that known as Lexan^R, sold by General Electric Company. It is a tough material, having high impact strength, high heat deflection temperature, good dimensional stability, as well as being self-extinguishing, and is easily fabricated. Acrylics, such as polymethylmethacrylate, are also widely used transparent plastics for glazing.

Attempts have been made to improve the abrasion-resistance of transparent plastics. For example, scratch-resistant coatings formed from mixtures of silica, such as colloidal silica or silica gel, and hydrolyzable silanes

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in a hydrolysis medium, such as alcohol and water, are known. U.S. Patents 3,708,225, Robert D. Misch et al, issued January 2, 1973, 3,986,997, Clark, issued October 19, 1976 and 3,976,497, Clark, issued August 24, 1976.

5 In Canadian Application Serial No. 339,539, November 9, 1979, coating compositions having improved resistance to moisture and humidity and ultraviolet light are disclosed. It was discovered therein that, in direct contrast to the teachings of U.S. Patent 3,986,997
10 compositions having a basic pH, i.e., 7.1-7.8, do not immediately gel but in fact provide excellent abrasion-resistant coatings on solid substrates.

The present invention offers a significant advantage over many of the heretofore known coating
15 compositions in that it does not require heat in order to initiate the cure reaction. The radiation cure system of the present invention expends considerably less thermal energy than conventional heat cure systems.

In copending Canadian Application Serial No.
20 376,679, May 1, 1981, the present applicant has disclosed a radiation curable hardcoating composition which requires the use of the acid hydrolysis product of an alkoxy functional silane. In another copending application, Serial No. 380,250, June 19, 1981, the present applicant
25 has provided a different radiation curable hardcoating composition which requires the combination of colloidal silica, acryloxy or glycidoxo functional silanes and non-silyl acrylates. Applicant's present invention, however, provides highly abrasion resistant coatings which require
30 neither alkoxy functional silanes of Serial No. 376,679 nor the acryloxy or glycidoxo functional silanes of Serial No. 380,250.

In fact, the coating compositions of the present invention are specific improvements over the coatings and
35 articles disclosed in U.S. Patent No. 4,198,465, Moore et

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al, April 15, 1980. The Moore et al disclosure teaches that certain very useful coatings and coated articles can be provided through the photoreaction of certain poly-functional acrylate monomers and resorcinol monobenzoate.

5 The Moore et al coatings use any of several well known UV radiation photosensitizers including ketones such as benzophenone. The Moore et al disclosure, however, failed to recognize that the improved coatings of the present invention could be provided by combining the

10 ketone-type photoinitiator with a hindered amine-type compound whereupon the photosensitized acrylate coating composition could be cured without the necessity of using resorcinol monobenzoate and without the necessity of an inert atmosphere (both of which are required by the

15 Moore et al disclosure), in order to provide suitable and sometimes improved hard coatings. The savings provided by the use of a non-inert atmosphere such as air can be substantial, and these savings can be provided by the present invention without derogating from the quality of

20 the hard coating composition or coated product.

Since ultraviolet light is one of the most widely used types of radiation because of its relatively low cost, ease of maintenance, and low potential hazard to industrial users, rapid photo-induced polymerizations

25 utilizing UV light rather than thermal energy for the curing of hard coatings offer several other significant advantages. First, faster curing coatings offer substantial economic benefits. Furthermore, heat sensitive materials can be safely coated and cured with

30 UV light without the use of thermal energy which could damage the substrate. Additionally, the essentially solvent free media reduce the necessity for expensive and time consuming pollution abatement procedures.

Thus, the advantages provided by the materials of the present invention are particularly *significant*

35 for a number of purposes. For example,

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polycarbonates are commercially important materials possessing excellent physical and chemical properties which are useful in a wide range of applications from non-opaque impact resistant sheets to shaped articles. 5 Generally, however, polycarbonates have rather low scratch resistance and are somewhat susceptible to attack by many common solvents and chemicals.

Previous efforts to overcome this low scratch resistance and susceptibility to attack by solvents have 10 included lamination procedures and applications onto the polycarbonate of a surface coating. Many of these prior art remedial efforts have been unsuccessful due to the incompatibility of the laminae and coating materials with the polycarbonate substrate. This incompatibility has 15 resulted in stress cracking and crazing of the polycarbonate, crack propagation into the polycarbonate as a result of the brittleness of the coating, and a reduction of the advantageous properties of the polycarbonate such as, for example, impact resistance, tensile strength, non- 20 opacity and elongation.

The prior art coatings for polycarbonates have included organopolysiloxanes, U.S. Patent No. 3,707,397, Gagnon, issued December 26, 1972; polyester-melamines or acrylic-melamines, U.S. Patent No. 3,843,390, Hudson 25 et al, issued October 22, 1974; and allyl resins, U.S. Patent No. 2,332,461. These types of prior art coatings are generally applied from solutions of inert solvents and are cured to final properties by baking at elevated temperatures. The disadvantages of such systems are 30 obvious. The heat curing requires a supply of thermal energy thereby adding to the cost of the system. Further, the thermal curing step is somewhat limited by the heat distortion temperature of the polycarbonate which is to be coated. Thus, in coating of polycarbonates, sheets of 30 35 mils and less generally cannot be coated and cured

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economically because of excessive warpage of the sheets during the thermal curing process.

U.S. Patent No. 3,968,305, Oshima et al, issued July 6, 1976, describes a synthetic shaped article having
5 a mar-resistant polymer surface layer integrated with the polymer surface body, said polymer surface layer consisting essentially of, in polymerized form, (a) 20 to 100 weight percent of a compound having a total of at least three acryloxy and/or methacryloxy groups linked with a straight
10 chain aliphatic hydrocarbon residue having not more than 20 carbon atoms, and (b) 0 to 80 weight percent of at least one copolymerizable mono- or diethylenically unsaturated compound. This type of a surface layer suffers from the fact that it generally has poor durability of adhesion after
15 prolonged exposure to weathering.

U.S. Patent No. 3,968,309, Matsuo et al, issued July 6, 1976, describes a molded article of plastic having on its surface a cured film of a coating material comprising at least 30% by weight of at least one polyfunctional
20 compound selected from the group consisting of polymethacryloxy compounds having a molecular weight of 250 to 800 and containing at least three methacryloyloxy groups in the molecule and polyacryloyloxy compounds having a molecular weight of 250 to 800 and containing at least
25 three acryloyloxy groups in the molecule. This patent, however, also teaches that this coating must contain from 0.01 to 5% by weight of a fluorine-containing surfactant in order for the coated article to be acceptable. This patent teaches that when the coating material contains
30 less than 0.01% by weight of the fluorine-containing surfactant, it is impossible to obtain a coated article having the requisite degree of surface hardness, surface smoothness, abrasion resistance and optical clarity. If the coating material contains more than 5% by weight of
35 said fluorine-containing surfactant, the adhesion between

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a cured film of the coating material and a molded substrate of plastic is unsatisfactory.

It has now been found that a coating composition containing certain specific polyfunctional acrylic monomers in combination with a blend of ketone and hindered amine photoinitiators provides excellent and durable UV cured coatings, especially for high strength plastic substrates such as polycarbonate, polyester, polymethylmethacrylate, and other polyacrylates, as well as polyamides, nylon and metalized plastic surfaces. These materials may be in films or sheets as well as in the form of molded parts. Thus, the present invention provides certain acrylate ester monomer based UV-cured coatings which adhere tenaciously and durably to the substrate, are compatible with the substrate, are mar, abrasion and solvent resistant, and maintain properties after prolonged exposure to weathering.

It is therefore an object of the present invention to provide ultraviolet light curable coating compositions providing improved mar and abrasion resistance which are curable under a non-inert atmosphere such as air.

It is another object to provide a UV curable coating comprising the photoreaction products of certain polyfunctional acrylate monomers and a blend of ketone-type and hindered amine-type photoinitiators.

It is another object to provide a process for providing abrasion resistant ultraviolet light curable coating compositions which are curable on rigid and flexible substrates, and which do not require an inert atmosphere for proper curing thereon.

It is still another object to provide articles of manufacture which are highly mar and abrasion resistant by virtue of having been coated with the coatings of the present invention which have been cured thereon.

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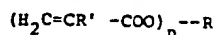
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Summary of the Invention

The present invention provides an abrasion resistant, durably adhered, ultraviolet light curable hardcoating composition which is curable in a non-inert atmosphere, and which comprises:

(A) at least one ultraviolet light curable (i.e. cross-linkable) polyfunctional acrylate monomer represented by the general formula



wherein n is an integer having a value of from 1 to 4, and R is selected from the group consisting of n valent aliphatic hydrocarbon residue, n valent aliphatic hydrocarbon residue containing at least one ether linkage, and n valent substituted hydrocarbon residue of either type, and R' is hydrogen or a lower alkyl radical such as methyl.

B The coating ^{composition} ~~composition~~ is completed by adding to ingredient (A) a blend of photoinitiators which have been discovered effective for crosslinking (A) to form the hard coatings of the present invention, upon exposure to ultraviolet radiation and without the necessity of an inert (e.g. N₂) blanketing atmosphere.

Description of the Invention

In accordance with the present invention, there may be provided a non-opaque, more specifically, a transparent, article having deposited on the surface thereof an adherent, mar, abrasion and chemical resistant non-opaque coating, said coating containing the photoreaction products of at least one UV curable polyfunctional acrylate monomer, and a blend of ketone and amine type photoinitiators as will be described below. The coating is obtained through the UV cure of a UV curable coating composition comprised of (i) at least one UV curable polyfunctional acrylate monomer, and (ii) the selected

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photoinitiator blend, under a non-inert atmosphere. An anti-weathering agent such as resorcinol monobenzoate, resorcinol dibenzoate, methyl resorcinol monobenzoate, and methyl resorcinol dibenzoate, and may be included if optionally desired.

5 To exemplify the practice of this invention, any of the aromatic polycarbonates can be employed. These are homopolymers and copolymers and mixtures thereof that are prepared by reacting a dihydric phenol with a carbonate precursor. Typical of some of the dihydric phenols that 10 may be employed in the practice of this invention are bisphenol-A (2,2-bis(4-hydroxyphenyl)propane), bis(4-hydroxyphenyl)methane, 2,2-bis(4-hydroxy-3-methylphenyl)propane, 3,3-bis(4-hydroxyphenyl)pentane, 2,2-bis(3,5-dichloro-4-hydroxyphenyl)propane, 2,2-bis(4,3,5-dibromo-4-hydroxyphenyl)- 15 propane, and bis(3-chloro-4-hydroxyphenyl) methane. Other dihydric phenols of the bisphenol type are also available and are disclosed in U.S. Patent Nos. 2,999,835, issued September 12, 1961 to Goldberg; 3,028,365, issued April 3, 20 1962 to Schnell et al; and 3,334,154, issued August 1, 1967 to Kim.

It is, of course, possible to employ two or more different dihydric phenols or a copolymer of a dihydric phenol with a glycol or with hydroxy or acid terminated 25 polyester, or with a dibasic acid in the event a carbonate copolymer or interpolymer rather than a homopolymer is desired for use in the preparation of the aromatic carbonate polymers of this invention. Also employed in the practice of this invention may be blends of any of the above 30 materials to provide the aromatic carbonate polymer.

To carbonate precursor may be either a carbonyl halide, a carbonate ester or a haloformate. The carbonyl halides which can be employed herein are carbonyl bromide, carbonyl chloride and mixtures thereof. Typical 35 of the carbonate esters which may be employed herein are diphenyl carbonate, di-(halophenyl) carbonates such as di-(chlorophenyl) carbonate, di-(bromophenyl) carbonate,

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di-(trichlorophenyl) carbonate, di-(tribromophenyl) carbonate, etc., di-(alkylphenyl) carbonate such as di(tolyl) carbonate, etc., di-(naphthyl) carbonate, di-(chloronaphthyl) carbonate, phenyl tolyl carbonate, chlorophenyl chloronaphthyl carbonate, etc., or mixtures thereof. The haloformates suitable for use herein include bis-haloformates of dihydric phenols (bischloroformates of hydroquinone, etc.) or glycols (bishaloformates of ethylene glycol, neopentyl glycol, polyethylene glycol, etc.). While other carbonate precursors will occur to those skilled in the art, carbonyl chloride, also known as phosgene, is preferred.

Also included are the polymeric derivatives of a dihydric phenol, a dicarboxylic acid and carbonic acid. These are disclosed in U.S. Patent No. 3,169,121, Goldberg, issued February 9, 1965.

The aromatic carbonate polymers of this invention may be prepared by employing a molecular weight regulator, an acid acceptor and a catalyst. The molecular weight regulators which can be employed in carrying out the process of this invention include monohydric phenols such as phenol, chroman-1, para-tertiarybutyl-phenol, para-bromophenol, primary and secondary amines, etc. Preferably phenol is employed as the molecular weight regulator.

A suitable acid acceptor may be either an organic or an inorganic acid acceptor. A suitable organic acid acceptor is a tertiary amine and includes such materials as pyridine, triethylamine, dimethylaniline, tributylamine, etc. The inorganic acid acceptor may be one which can be either a hydroxide, a carbonate, a bicarbonate, or a phosphate of an alkali or alkaline earth metal.

The catalysts which are employed here can be any of the suitable catalysts that aid the polymerization of bisphenol-A with phosgene. Suitable catalysts include tertiary amines such as, for example, triethylamine,

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tripropylamine, N,N-dimethylaniline, quaternary ammonium compounds such as, for example, tetraethylammonium bromide, cetyl triethyl ammonium bromide, tetra-n-heptyl-ammonium iodide, tetra-n-propyl ammonium bromide, 5 tetramethyl ammonium chloride, tetramethyl-ammonium hydroxide, tetra-n-butyl-ammonium iodide, benzyltrimethylammonium chloride and quaternary phosphonium compounds such as, for example, n-butyltriphenyl phosphonium bromide and methyltriphenyl phosphonium bromide.

10 Also included therein are branched polycarbonates wherein a polyfunctional aromatic compound is reacted with the dihydric phenol and carbonate precursor to provide a thermoplastic randomly branched polycarbonate.

These polyfunctional aromatic compounds contain 15 at least three functional groups which are carboxyl, carboxylic anhydride, or haloformyl groups or mixtures thereof. Examples of these polyfunctional aromatic compounds which may be employed in the practice of this invention include: trimellitic anhydride, trimellitic 20 acid, trimellityl trichloride, 4-chloroformyl phthalic anhydride, pyromellitic acid, pyromellitic dianhydride, mellitic acid, mellitic anhydride, trimesic acid, ~~benzophenonetetracarboxylic~~ benzophenonetetracarboxylic acid, benzophenonetetracarboxylic anhydride and the like. The preferred polyfunctional 25 aromatic compounds are trimellitic anhydride or trimellitic acid, or their haloformyl derivatives.

Also included herein are blends of a linear polycarbonate and a branched polycarbonate.

It is to be understood that the utility of the 30 coating composition of the present invention is not limited to the polycarbonates described above. There are numerous other classes of substrates which may be suitably rendered mar and abrasion resistant by the coatings and processes disclosed herein. Among these 35 other substrates are such sheet, film and molded substrates

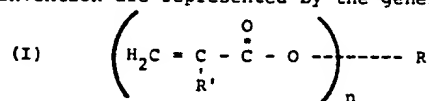
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as polyester and polymethylmethacrylate and other high strength films such as polyacrylates, polyamides, nylon and plastic surfaces which have been metalized by such techniques as sputtering, electroplating and vapor
5 deposition. Metal surfaces such as aluminum may also be coated.

The polyfunctional acrylate ester monomers of the present invention are represented by the general formula



10 wherein n is an integer from 1 to 8, preferably from 1 to 6, and more preferably from 1 to 4; and R is a n functional hydrocarbon residue, a n functional substituted hydrocarbon residue, a n functional hydrocarbon residue containing at least one ether
15 linkage, and a n functional substituted hydrocarbon residue containing at least one ether linkage, and R' is hydrogen or a lower alkyl radical such as methyl.

Preferred n functional hydrocarbon residues are the n functional aliphatic, preferably saturated
20 aliphatic, hydrocarbon residues containing from 1 to about 20 carbon atoms and the n functional aromatic hydrocarbon residues containing from 6 to about 10 carbon atoms.

Preferred n functional hydrocarbon residues containing at least one ether linkage are the n functional aliphatic hydrocarbon residues, preferably saturated aliphatic hydrocarbon residues, containing from 1 to about 5 ether linkages and from 2 to about 20 carbon
25 atoms.

30 Preferred n functional substituted hydrocarbon residues are the n functional aliphatic hydrocarbon residues, preferably the saturated aliphatic hydrocarbon

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residues, containing from 1 to about 20 carbon atoms,
and the n functional aromatic hydrocarbon residues
containing from 6 to about 10 carbon atoms which contain
substituent groups such as the halogens, i.e., fluorine,
5 chlorine, bromine and iodine, hydroxyl, --COOH, and --COOR'
groups wherein R' represents alkyl groups containing from
1 to about 6 carbon atoms.

Preferred n functional substituted hydrocarbon
residues containing at least one ether linkage are the n
10 functional aliphatic, preferably saturated aliphatic,
hydrocarbon residues containing from 2 to about 20 carbon
atoms and from 1 to about 5 ether linkages which contain
substituent groups such as the halogen hydroxyl, --COOH,
and --COOR' groups wherein R' is as defined above.

15 It is to be understood that where substituent
groups are present, they should be such that they do not
unduly hinder or interfere with the photocure of the
polyfunctional acrylic monomers.

The more preferred polyfunctional acrylic
20 monomers are those represented by formula I wherein R is
selected from the group consisting of an n functional
saturated aliphatic hydrocarbon residue containing from
1 to about 20 carbon atoms, a hydroxyl substituted n
functional saturated aliphatic hydrocarbon residue
25 containing from 1 to about 20 carbon atoms, an n
functional saturated aliphatic hydrocarbon residue
containing from about 2 to about 20 carbon atoms and from
about 1 to about 5 ether linkages, and a hydroxyl
substituted n functional saturated aliphatic hydrocarbon
30 residue containing from 2 to about 20 carbon atoms and
from 1 to about 5 ether linkages.

The preferred polyfunctional acrylate ester
monomers are those wherein R is an n functional saturated
aliphatic hydrocarbon, ether, or polyether radical, with
35 those monomers wherein R is an n valent saturated

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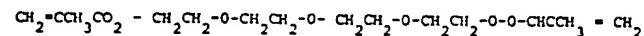
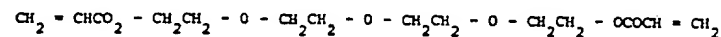
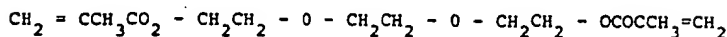
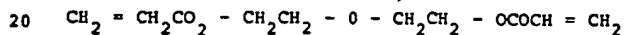
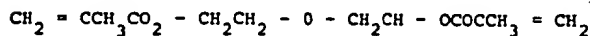
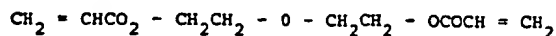
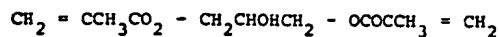
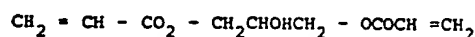
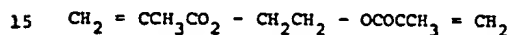
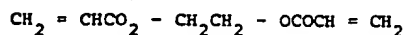
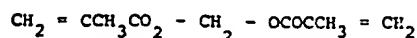
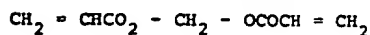
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aliphatic hydrocarbon radical being more preferred.

More particularly, the difunctional acrylic monomers, or diacrylates, are represented by formula I wherein n is 2; the trifunctional acrylic monomers, or triacrylates, are represented by formula I wherein n is 3; and the tetra-functional acrylic monomers, or tetraacrylates, are represented by formula I wherein n is 4. Illustrative of suitable polyfunctional acrylate ester monomers of formula I are those listed below in

TABLE I.

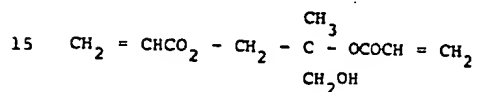
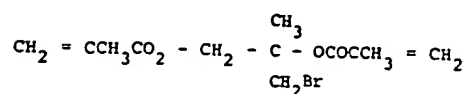
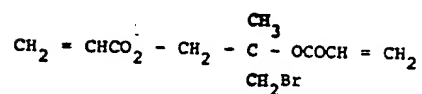
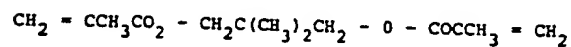
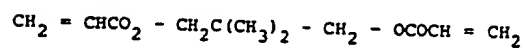
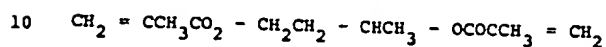
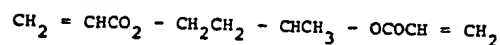
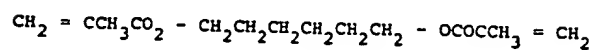
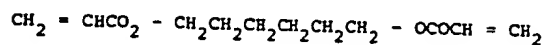
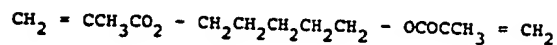
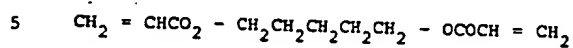
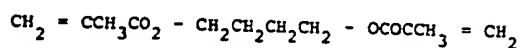
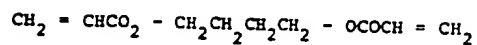
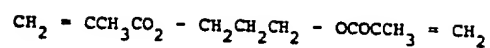
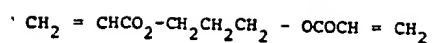
TABLE I



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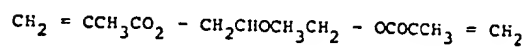
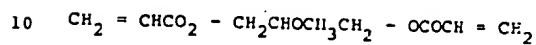
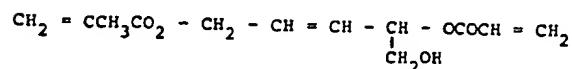
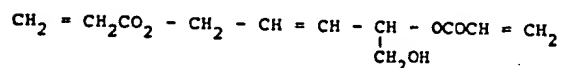
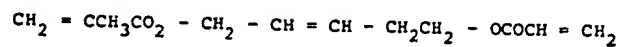
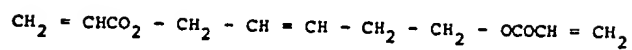
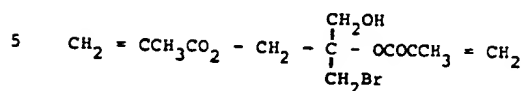
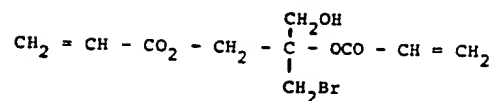
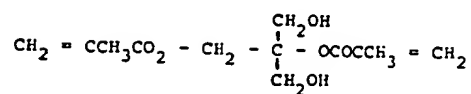
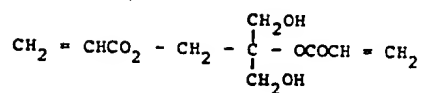
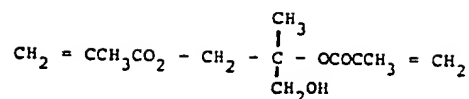
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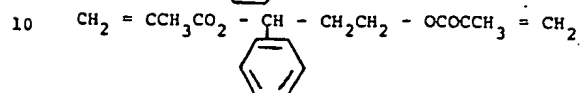
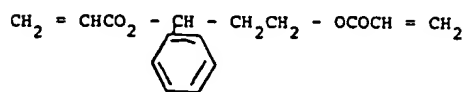
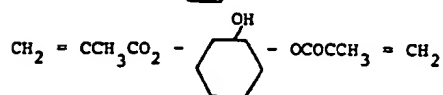
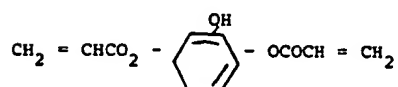
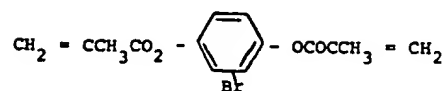
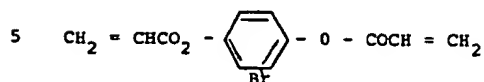
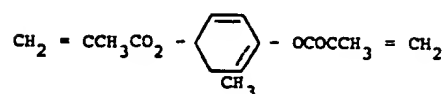
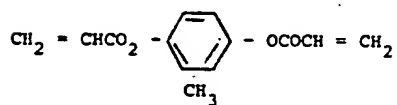
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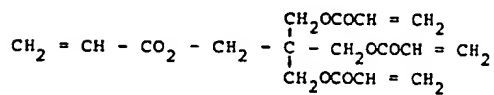
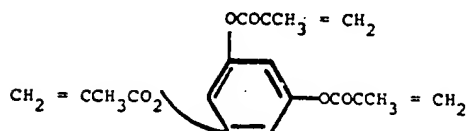
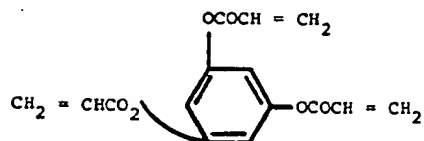
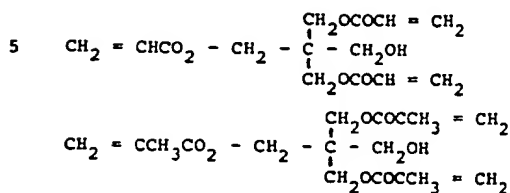
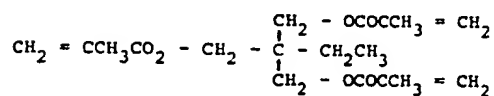
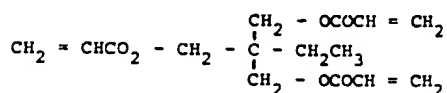
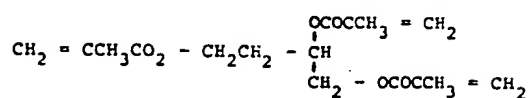
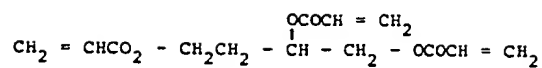
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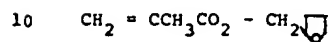
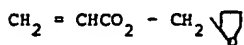
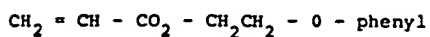
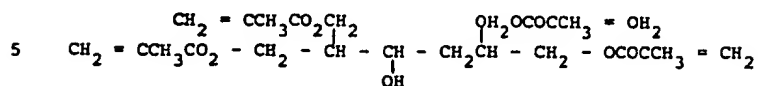
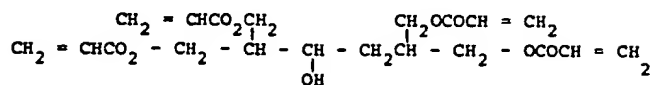
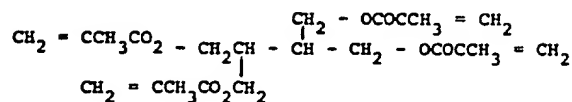
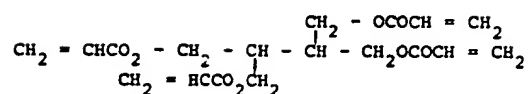
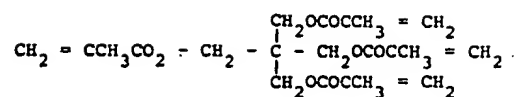
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These polyacrylate esters and their production are well known to those skilled in the art. One method of producing the di-, tri-, and tetraacrylate esters involves reacting acrylic acid with a di-, tri-, or tetrahydroxyl compound to produce the diester, triester or tetraester. Thus, for example, acrylic acid can be reacted with ethylene glycol to produce ethylene glycol diacrylate.

Although the coating compositions may contain only one of said polyfunctional acrylate monomers, preferred coating compositions contain a mixture of two polyfunctional monomers, preferably a diacrylate and a triacrylate. When the coating compositions contain a mixture of acrylate monomers, it is preferred that the ratio, by weight, of the diacrylate to the triacrylate be from about 30/70 to about 70/30. Exemplary mixtures of diacrylates and triacrylates include mixtures of hexanediol diacrylate with pentaerythritol triacrylate, hexanediol diacrylate with trimethylolpropane triacrylate, diethyleneglycol diacrylate with pentaerythritol triacrylate, and diethyleneglycol diacrylate with trimethylolpropane triacrylate.

While the corresponding coatings may likewise contain the ultraviolet light reaction product of a single polyfunctional acrylate monomer, coatings containing the photoreaction product of two polyfunctional acrylate monomers, preferably a diacrylate and a triacrylate, are preferred.

Generally, the coating composition contains from about 70 to about 99 percent of the polyfunctional acrylate or acrylates. The UV cured coating contains from about 70 to about 99 weight percent of the photoreaction products of the polyfunctional acrylate monomer or mixture of acrylate monomers present in the coating composition.

The photocurable coating compositions also contain a photosensitizing amount of photosensitizer, i.e., an

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amount effective to effect the photocure of the coating composition. Generally, this amount is from about 0.1% to about 10% by weight and preferably from about 0.1% to about 5% by weight of the photocurable coating composition.

5 It has been discovered through the present invention that certain blends of ketone-type and hindered amine type materials are photoinitiators which are effective for crosslinking the above described polyfunctional acrylates to form suitable hard coatings
10 upon exposure to UV radiation. It is preferred that the ratio, by weight, of the ketone compound to the hindered amine compound be from, approximately, 80/20 to 20/80. Ordinarily, 50/50 or 60/40 mixtures are quite satisfactory.

Among the particularly preferred ketone-type
15 compounds are those selected from the group consisting of: benzophenone, and other acetophenones, benzil, benzaldehyde and o-chlorobenzaldehyde, xanthone, thioxanthone,
20 2-chlorothioxanthone, 9,10-phenanthrenequinone, 9,10-anthraquinone, ethylbenzoin ether, isopropyl benzoin ether,
25 a, a-diethoxyacetophenone, 1-phenyl-1 2-propanediol-2-o-benzoyl oxime, and a,a - dimethoxy-a-phenylacetophenone,

In the above formulas, lower case a represents configurations of radicals in the alpha position.

30 Among the particularly preferred hindered amine-type compounds are those selected from the group consisting of:

methyldiethanol amine,
ethyldiethanol amine,
35 dimethylethanol amine,

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diethyl ethanol amine,
triethanol amine,
dimethyl amino ethylbenzoate,
ethyl-3-dimethyl amino benzoate,
5 4-dimethyl amino benzophenone,
4-diethyl amino benzophenone,
4,4' -bis (diethylamino) benzophenone,
4,4' -bis (dimethylamino) benzophenone,
N, N-diethyl aniline,
10 phenyl methyl ethanol amine,
phenyl ethyl ethanol amine,
phenyl diethanol amine, and
N,N,N',N' -tetramethyl - 1,3 -butanediamine.

The coating compositions of the instant invention

15 may also optionally contain resorcinol monobenzoate. The
resorcinol monobenzoate is present in an amount, based upon
the weight of the coating composition, exclusive of any
additional solvent which may optionally be present, of
from about 1 to about 20 weight percent, preferably from
20 about 3 to about 15 weight percent. The UV cured coating
contains from about 1 to about 20% by weight of the
photoreaction products of resorcinol monobenzoate, which
products are formed during the UV cure of the UV curable
coating composition if the resorcinol monobenzoate is
25 utilized.

The coating compositions of the instant invention
may also optionally contain various flattening agents,
surface active agents, thixotropic agents, UV light
absorbers and dyes. All of these additives and the use
30 thereof are well known in the art and do not require
extensive discussions. Therefore, only a limited number
will be referred to, it being understood that any
compounds possessing the ability to function in such a
manner, i.e., as a flattening agent, surface active agent,
35 UV light absorber, and the like, can be used so long as

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they do not deleteriously affect the photocuring of the coating compositions and do not adversely affect the non-opaque character of the coating.

The various surface-active agents, including
5 anionic, cationic and nonionic surface-active agents are described in Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 19, Interscience Publisher, New York, 1969, pp. 507-593, and Encyclopedia of Polymer Science and Technology, Vol. 13, Interscience Publishers, New
10 York, 1970, pp. 477-486.

In the practice of the present invention, the photocurable coating compositions are first compounded by adding together the polyfunctional acrylic monomer or mixtures thereof, the UV photosensitizer blend, and,
15 optionally, any of the other aforementioned additives. Additionally, if so desired to reduce the viscosity of the coating formulation, an organic solvent, such as an alcohol, may optionally be incorporated into the formulation. Generally, the amount of solvent, if any,
20 present should be such that evaporation of the solvent occurs before any deleterious effect on the substrate. The various components are thoroughly mixed so as to form a generally homogeneous coating compositions. A thin, uniform coating of the coating solution is then
25 applied onto the substrate by any of the known means such as dipping, spraying, rollcoating and the like. The coating is then cured in a non-inert, e.g., air, atmosphere, by UV irradiation which can have a wavelength of from 1849 A. to 4000A. The lamp systems used to generate such
30 radiation can consist of ultraviolet lamps which can consist of discharge lamps, as for example, xenon, metallic halide, metallic arc, such as low or high pressure mercury vapor discharge lamp, etc., having operating pressures of from as low as a few milli-torr up to about
35 10 atmospheres. By curing is means both polymerization

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of the polyfunctional acrylic monomers and cross-linking of the polymers to form hard, non-tacky coatings.

PREFERRED EMBODIMENT OF THE INVENTION

5 In order to more fully and clearly describe the invention, it is intended that the examples be considered as illustrative rather than limiting the invention disclosed and claimed herein. All parts are by weight.

EXAMPLE 1

10 An aromatic polycarbonate is prepared by reacting 2,2-bis(4-hydroxyphenyl) propane and phosgene in the presence of an acid acceptor and a molecular weight regulator. The product is then fed to an extruder, which extruder is operated at about 265°C and the extrudate is comminuted into pellets.

15 The pellets are then injection molded at about 315°C into test panels of about 4 in. by 4 in. by about 1/8 in. thick. The test panels are subjected to an abrasion test, Gardner Impact Test and an adhesion test.

20 The abrasion test in one wherein test panels having a 17/64th inch diameter hole cut in the center are subjected to a Taber Abraser. The Taber Abraser is equipped with CS-10F wheels which are resurfaced every 500 cycles by abrading for 25 cycles on a S-111 refacing disc. The weights used in combination with the CS-10F
25 wheels are 500 gm weights. Initial measurements of % Haze are made at four places around the future wear track of the sample using a Gardner Hazemeter. The sample is abraded for 500 cycles, cleaned with warm soap and water and dried by blowing compressed air across the sample, and the %
30 Haze is remeasured at the same four places. The four differences in % Haze are calculated and averaged to give the % Haze. The Δ% Haze of this uncoated sample is generally between 45 to 50.

The scribed adhesion test consists of using a

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B 5 multiple blade tool to cut parallel grooves through the coating and into the substrate. The test panel is then rotated 90° and the cutting process is repeated, thereby leaving a grid pattern consisting of 1 mm squares cut into the coating. An adhesive tape such as 3M's Scotch 710 is applied over the cross hatched area and quickly pulled off. A sample fails the adhesion test if any of the squares are pulled off by the tape. This test is repeated three times.

10 Examples 2,3, and 4 are comparative examples of unsuccessful hardcoating compositions utilizing polyfunctional acrylate monomers as basic ingredients.

EXAMPLE 2

15 A coating composition was prepared by combining 150 parts of hexanedioldiacrylate (HDDA), 150 parts of trimethylolpropanetriacrylate (TMPTA), 2 parts of benzophenone, 2 parts of dimethylethanol amine, and one part of a surface active agent BYK-300 produced by Mallinckrodt Chemical Co. of New Jersey. A film of about 0.15 mil of this mixture was coated on a polycarbonate panel produced in accordance with example 1. The coated panel was passed thorough a PPG Model QC 1202 UV-processor under an air atmosphere, where the conveyer speed was 20 feet/minute. Two passes through the system resulted in a coating which was tacky and undercured.

25 EXAMPLE 3

A coating composition was formulated by combining 200 parts diethylene glycol diacrylate, 200 parts trimethylolpropanetriacrylate, 2 parts benzophenone, 1.5 parts methyldiethanolamine, and one part BYK-300. 30 This mixture was coated on a polycarbonate test panel which was then twice passed through the PPG UV-processor under an air atmosphere. The resulting coating was tacky and not fully cured.

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EXAMPLE 4

A coating mixture was formulated by combining 200 grams hexanedioldiacrylate, 200 grams trimethylolpropanetriacrylate, 4 grams diethoxyacetophenone, 20
5 grams resorcinol monobenzoate, and 2 grams BYK-300. A film of about 0.2 mils was applied to a Lexan^R polycarbonate panel and passed 5 times through the PPG 1202 UV-Processor under a nitrogen blanket of 15 psi and at a conveyor speed of 20 ft./min. The resulting coating was
10 tacky, had cracks and was hazy.

The remaining examples demonstrate the successful hard coating compositions of the present invention.

EXAMPLE 5

A coating mixture was prepared by combining 100
15 parts of hexanedioldiacrylate, 100 parts of trimethylolpropanetriacrylate, 4 parts by weight of benzophenone, 4 parts by weight of methyldiethanolamine, and 1 part by weight of surface active agent BYK-300. This coating composition was applied to a polycarbonate panel and was
20 then passed through a PPG 1202 UV-processor in an air atmosphere where the conveyer speed was 20 ft/min. One pass through this system resulted in a coating which was hard and tack-free.

EXAMPLE 6

A coating mixture was prepared by combining 100g
25 of hexanedioldiacrylate, 100g of trimethylolpropanetriacrylate, 4g of benzophenone, 4g of methyldiethanolamine, 1g of BYK-300 and 10g of resorcinol monobenzoate. This mixture was coated on Lexan^R and passed through a UV-Processor as
30 in Example 2. The coated Lexan^R was subjected to the afore-described abrasion and scribed adhesion tests and the results are set forth in Table II.

EXAMPLE 7

A coating composition was made by combining
35 200 g of diethylene glycol diacrylate, 4g of benzophenone, 4g of methyldiethanol amine, and 1 g of BYK-300. This

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coating was applied to a Lexan^R panel and passed through a UV-Processor as in Example 2. The coated Lexan panel was also subjected to the afore-described abrasion and scribed-adhesion tests and the results are set forth in

5 Table II.

EXAMPLE 8

A coating composition was formulated by combining 100 g of trimethylolpropanetriacrylate, 2 g of benzophenone, 2 g of methyldiethanolamine, and 0.5 g of BYK-300. A film of about 0.2 mils thickness was applied to a Lexan^R sheet and passed through a UV-Processor as in Example 2. The coated Lexan^R panel was subjected to the afore-described abrasion and scribed adhesion tests and the results are set forth in Table II.

15 EXAMPLE 9

A coating composition was formulated by combining 250 g of diethylene glycol diacrylate, 250 g of trimethylolpropane triacrylate, 10g of benzophenone, 10g of methyldiethanolamine, and 2.5 g of BYK-300. This material was coated on a Lexan^R panel and passed through a UV-Processor as in Example 2. The results are set forth in Table II.

TABLE II

| 25 <u>Example No.</u> | <u>Adhesion Test</u> | <u>Δ H500</u> |
|-----------------------|----------------------|---------------------------------|
| 5 | pass | 24.6 |
| 6 | pass | 28.5 |
| 7 | pass | 23.3 |
| 8 | pass | 21.2 |
| 30 9 | pass | 19.2 |

Those skilled in the art will recognize that the Δ H500 haze data given in Table II represents coated articles having excellent abrasion resistance.

The foregoing example demonstrate that it is possible to provide air curable coating composition through the particular combination of polyfunctional acrylates and

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blended photoinitiators described above. These coatings
and coated articles also possess such other desirable
properties as optical clarity, durability of adhesion,
non-degradation of the properties of the substrate, and
5 protection of the substrate from the ^{deleterious} deleterious effects
of prolonged exposure to UV.

Although specific embodiments of the invention
have been described, it should not be limited to the
particular compositions and articles described herein,
10 but is intended to include all modifications that may be
made which, pursuant to the patent statutes and laws, do
not depart from the spirit and scope of the invention.

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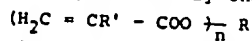
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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for providing an abrasion resistant,
5 durably adhered, ultraviolet light curable hard coating composition which is curable in a non-inert atmosphere, consisting essentially of the steps of:

(1) mixing

10 (A) at least one ultraviolet light cross-linkable polyfunctional acrylate monomer represented by the general formula



15 wherein n is an integer having a value of from 1 to 4, R is selected from the group consisting of substituted or unsubstituted n valent aliphatic hydrocarbon residue, n valent aliphatic hydrocarbon residue containing at least one ether linkage, and substituted n valent aliphatic hydrocarbon residue containing at least one
20 ether linkage, and R' is selected from hydrogen or lower alkyl radicals; and

25 (B) at least approximately 4.0% by weight to about 10% by weight of a photoinitiator comprised of a blend of (i) at least 2.0% by weight of one or more ketones and (ii) at least 2.0% by weight of one or more hindered amines, wherein said photoinitiator blend is effective for cross-linking (A) upon exposure to ultraviolet radiation;

30 (2) applying said mixture from (1) to a substrate; and

(3) curing said hard coating composition by exposure to an amount of ultraviolet radiation effective for cross-linking acrylate monomer (A).

- 35 2. A process as in claim 1 wherein said ketone is selected from the group consisting of:

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- 5 benzophenone, acetophenone, benzil,
benzaldehyde, o-chlorobenzaldehyde,
xanthone, thioxanthone, 2-chlorothioxanthone,
9,10-phenanthrenequinone,
9,10-anthraquinone,
ethylbenzoin ether,
isopropyl benzoin ether,
 α, α -dimethoxy- α -phenylacetophenone,
 α, α -diethoxyacetophenone, and
10 1-phenyl-1,2-propanediol-2-o-benzoin oxime.
3. A process as in claim 2 wherein said
hindered amine is selected from the group consisting of:
- 15 methyl-diethanol amine,
ethyl-diethanol amine,
dimethylethanol amine,
diethylethanol amine,
triethanol amine,
dimethylamino ethylbenzoate,
ethyl-3-dimethyl amino benzoate,
20 4-dimethyl amino benzophenone,
4-diethyl aminobenzophenone,
4,4'-bis(diethylamine) benzophenone,
4,4'-bis(dimethylamine) benzophenone,
N,N-diethyl aniline,
25 phenyl methyl ethanol amine,
phenyl ethyl ethanol amine,
phenyl diethanol amine, and
N,N,N',N'-tetramethyl-1,3-butanediamine.
4. A process as in claim 1 further consisting
30 essentially of the step of mixing an ultraviolet light
screening agent into said hard coating composition.
5. A process as in claim 4 wherein an anti-
weathering agent is used is selected from resorcinol mono-
benzoate, resorcinol dibenzoate, methyl resorcinol mono-
35 benzoate and methyl resorcinol dibenzoate.
6. A process as in claim 1 further consisting
essentially of a surface active agent.

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7. A process as in claim 6 wherein said photoinitiator blend consists essentially of benzophenone and methyldiethanol amine.

8. A process as in claim 1 wherein said
5 composition contains a mixture of hexanediol diacrylate and trimethylolpropane triacrylate monomers.

9. A process as in claim 1 wherein said non-inert atmosphere is air.

*

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